

## **DISPERSIONS OF NANOCCLAYS IN POLYMER MELTS.**

### **FIELD OF THE INVENTION**

001. This invention pertains to processes for dispersing additives into a polymer melt, and products made thereby. In particular the invention pertains to a process for incorporating thermally sensitive additives without degrading the additive or compromising its physical structure.

### **BACKGROUND OF THE INVENTION**

002. Additives are often added to polymer resins to improve their performance (mechanical, chemical) or their physical appearance (color), reduce their degradation sensitivity, or lower their cost, or any or all of the above combined. Sometimes, a certain additive that would be particularly suited for a given polymer, cannot be used for that particular polymer, because its introduction into the melt stream, at the conventional extrusion temperatures for that particular polymer, would actually degrade or reduce the performance of the filler at that temperature.

003. An example of a thermally sensitive additive is the filler Alumina Trihydrate (ATH or hydrated alumina) which is the most frequently used flame retardant in the world. This filler is a non-toxic, non-corrosive, flame retardant, smoke suppressant and is commonly used in elastomeric applications. On heating to 200°C, ATH decomposes into 66% alumina and 34% water. This irreversible reaction is, in part, what makes ATH an effective flame retardant. This thermal instability is also the reason why ATH cannot be used as a flame retardant in many polymers such as polyethylene terephthalate which need to be processed at temperatures well above 200°C.

004. An example of a thermally sensitive additive is wood flour. Wood flour is a low cost filler that degrades when introduced at melt temperatures above 200°C. This additive is therefore not normally suitable for incorporation into polymers which require high processing temperatures. In fact, its use is limited to mixing with polyethylene or polypropylene, both of which can be processed at temperatures of below 200°C. For example this additive is currently

processed with polypropylene at 190°C, just slightly below the wood flour degradation temperature using high melt flow index resins or with processing aids for reducing the plastic melt viscosity. Processing at such low temperatures also requires lower throughputs than are possible at the temperatures that are more typical of processing. Low throughputs are used in order to avoid local shear induced heating of the polymer and melt fracture. The industry would therefore welcome a process that allowed the user to mix wood flour with resins at throughputs that are more typical of processing of the polymer alone, and also eliminate the use of additives to lower viscosity or reduce degradation by melt fracture.

005. An example of an additive that loses its performance (in this case electrical conductivity) at high extrusion melt temperature is polyaniline powder. Most available polyaniline compositions can only withstand temperatures of 230-240°C for short periods of time (5-10 minutes) without significant change in electrical properties. For that reason, polyaniline can only be blended with commodity polymers such as polyethylene, polypropylene, polystyrene and different types of thermoplastic elastomers. In order to expand polyaniline applications, the industry is currently looking for ways to achieve compatibility with other matrixes (polymer), which normally requires high processing temperatures.

006. The use of organically modified clays, sometimes referred to as intercalates, organoclays, or nanoclays produced by a cation exchange reaction between the clay and an alkylammonium salt, is known in the prior art. In U.S. patent numbers 6,656,995 and 6,583,209 to Equistar, and application publication number 20030130399 also to Equistar, is disclosed the use of organoclays to enhance the melt strength of polyethylene and its copolymers.

007. These publications disclose that separating the adjacent platelets in nanoclays is desirable for the properties of the nanoclay plus polymer blend, and that alkylammonium cations exchanged into and between the clay platelets increase the interlayer spacing between adjacent platelets and render the hydrophilic clays organophilic and thus more easily dispersed in polyolefin resins.

Compared to conventional filled polyolefin compositions, polyolefins filled with the intercalated organoclays have improved physical properties at similar loading levels.

008. These publications also assert that compatibilizing agents are commonly employed to facilitate incorporation of modified clays into non-polar polymers, such as polyolefins, during melt compounding. Compatibilizers are generally maleic anhydride grafted polymers employed at a weight ratio of 3:1 (compatibilizer:organoclay). While polyolefin composites have been prepared using ratios of compatibilizer to organoclay as low as 1:1, the lower ratios are generally considered to be less desirable and, therefore, are typically avoided. For example, Hasegawa, et al., in an article entitled "Preparation and Mechanical Properties of Polypropylene-Clay Hybrids Using a Maleic Anhydride Modified Polypropylene Oligomer," JAPS 67, 87 (1998), observe that as the ratio of compatibilizer to organically modified clay is increased, the particles of the silicate layers become smaller and are dispersed more uniformly so that the reinforcement effect of the clays is increased.

009. Lim, et al., in their article "Phase Morphology and Rheological Behavior of Polymer/Layered Silicate Nanocomposites," Rheol Acta 4: 220-229 (2001), report the fabrication of nanocomposites with organophilic modified clays and polyethylene base resins grafted with 0.8 weight percent maleic anhydride. The nanocomposites are formed by melt-mixing.

0010. In the particular case of nanoclay fillers for plastics, the binder or compatibilizing agent that is often chemically attached to the nanoclay particle can be itself thermally sensitive to temperature and can degrade at the high temperature of melt flow required for the blending or dispersing operation. One example of such thermally sensitive coating is seen in the case of natural montmorillonite nanoclay modified/coated with a quaternary ammonium salt (manufactured namely by Southern Clay Products). This nanoclay is an additive for plastics used to improve various physical properties such as stiffness, heat deflection temperature and barrier properties. The purpose of the coating on the nanoparticle is to improve its dispersion and tendency to exfoliation (i.e.

separation of platelets), which are intrinsically related to its physical performance. The thermal stability of the nanoclay is determined by the thermal stability of the ammonium salt treatment. The thermogravimetric analysis (TGA) of the nanoclay shows that the ammonium ion salt coating on the nanoclay starts to decompose around 200°C, therefore processing of this nanoclay must be performed below that temperature. For that reason, nanoclay fillers with a relatively inexpensive coating cannot be dispersed into polymers which require processing temperature higher than 200°C. The cost of the coating goes up as more expensive coatings are developed to be able to withstand processing temperatures. Because of the benefits associated with nanoclays, the industry would be very much interested in a process which would allow them to use this advantageous filler in a greater number of matrixes/polymers and with the least expensive coating. This advantage can only be achieved by introducing the nanoclay into the polymer at temperatures that are below the conventional temperature range at which polymers are processed.

0011. Examples abound in the patent literature of other coatings on particles that are intended for use on fillers that are then used to modify the properties of a polymer matrix. U.S. 4,495,245 to DuPont is an early example of a disclosure of the need to coat inorganic fillers with, in that case, a vinyl alcohol polymer and cationic melamine coating.

0012. U.S. 4,740,538 to Engelhard Corp. is an example of the use of coated minerals in polyamides.

0013. U.S. 5,028,482 to ECC International, discloses an inorganic filler coated with a latex.

0014. The industry would therefore like a method for being able to incorporate additives of all types into polymer melts that allows for such incorporation to take place at lower temperatures than are commonly utilized for melt processing. Such a process would induce fewer changes in the morphology or degradative state of the additive in the final part which comprises the polymer melt and additive.

## **BRIEF SUMMARY OF THE INVENTION**

0015. The present inventor has discovered that it is possible to incorporate additives into polymers at temperatures significantly below the temperature that would normally be considered to be a lower limit for processing for said polymers. The lower temperature of incorporation means that additives that would otherwise be unsuitable for use in a particular polymer matrix because of processing limitations, now have utility in those polymers.

0016. The present invention describes a method to allow the dispersion of additives such as fillers, coupling agents or binders and other fine particles into the melt stream of a polymer by blending the additives with a polymer melt when it is a molecularly disentangled state. The present invention is also advantageous for dispersion of nanoparticles into polymer melts. The dispersion of other particles that would be normally susceptible to sedimenting, agglomeration, clustering, or creation of nodules, instead of finely dispersing at their most elementary particle level, is also now possible.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

0017. Figure 1 shows a process flow schematic of an embodiment of the invention in which a polymer is passed through a disentanglement process and on to a blending station for melt blending with an additive.

0018. Figure 2 shows a process flow schematic of the preferred embodiment of the reaction in which a multi stage disentanglement process is used.

### **DETAILED DESCRIPTION OF THE INVENTION**

#### **Definitions**

0019. The invention can be best understood by reference to the following definitions.

0020. By "additive" is meant a material that is added to a polymer, normally into the molten phase of the polymer, in such a way that the material is dispersed in the polymer matrix when the matrix is cooled and has solidified. Dispersion can be at a molecular level, which would be the case, for example, when a compound is dispersed that is soluble in the polymer matrix. Dispersion

can also be at a particulate level, as for example, when a pigment or filler is added to a polymer matrix. In both examples of dispersion, the additive is distributed evenly over the polymer matrix in some region.

0021. An additive as used here can also refer to a macromolecular material such as a polymer or an oligomer, or other compound that can be melt blended into the polymer.

0022. By "polymer chains" is meant the molecular backbone of the polymer. In a linear polymer, the backbone comprises the longest sequence of connected atoms in any given molecule. In a highly branched polymer such as low density polyethylene (LDPE), the backbone comprises all of the carbon atoms in a given molecule. The "family" of a polymer refers to the monomers that go to make up the polymer chain. For example, two polymer chains of different molecular weights, and hence melt flow indices, that comprise the same monomers in their backbones, are of the same family. The present invention is useful for blending polymers of the same and different families.

0023. The term "macromolecular disentanglement" refers to the process of either partially or completely removing entanglements among polymer chains in a given polymer sample. Both US 5,885,495 and US 6,210,030, and both to Ibar and both incorporated herein by reference in their entirety, disclose use of disentanglement to control, and essentially lower, the viscosity on a polymer melt. These patents also disclose the disentanglement processing window parameters which optimize the efficiency of the viscosity control invention. Other publications by Ibar on the subject of disentanglement are also provided as reference: J.P. Ibar, SPE ANTEC Proceedings, paper 224 (1999), J.P. Ibar, SPE ANTEC Proceedings, paper 225 (1999), J.P. Ibar, SPE ANTEC Proceedings, paper 226 (1999), J.P. Ibar, SPE ANTEC Proceedings, paper 480(2001), J.P. Ibar, SPE ANTEC Proceedings, paper 481 (2001), and J.P. Ibar, SPE ANTEC Proceedings, paper 482 (2001). Polymer that has been disentangled can be solidified by cooling, and stored for future use, where it can be re-melted and supplied to a process.

0024. The term "Tek Flow Processor" refers to a commercial apparatus of the embodiment of the invention of U.S. 6,210,030 in which the viscosity of a polymer is controlled by disentanglement of the polymer chains that the polymer comprises. The Tek Flow Processor is available from Stratek Plastic Ltd. (Dublin, Ireland) and SPRL Inc. (Wallingford, CT, USA).

0025. The term "melt blending" refers to the process by which an additive, which may be soluble or insoluble in a polymer matrix, is dispersed in a matrix by application of a combination of heat and shear to an un-dispersed mixture of the additive and the polymer. Melt blending can take place in various types of equipment, which are well known to one skilled in the art pertaining to this invention. For the purposes of this invention, such equipment can include, but is not limited to, single and twin screw extruders, for example the equipment made by Farrel Corporation (Ansoma, CT), Brabender type mixtures operated in batch or continuous mode (Brabender Co., Germany) and ribbon type mixers.

0026. A "blend" is a product that comprises a polymer and an additive that has been dispersed therein.

0027. By "polymer melt" is meant a polymeric material which is at a temperature that is above the first order phase transition commonly known in the art as "the melt temperature" or  $T_m$ . A polymer melt is generally shaped into a useful article at a temperature that makes the viscosity of the melt amenable to processing in whatever equipment is suitable for the process. A "molecularly disentangled polymer melt" is a melt that has been through the process of macromolecular disentanglement. Such a melt can be supplied within a process as one of a number of sequential process steps by online disentanglement of a polymer melt using suitable equipment, or it can be supplied in a previously disentangled state, for example in pellet form, and melted in conventional equipment.

0028. "Conventional processing conditions" refers to the combination of temperature and throughput conditions that would be commonly used by one skilled in the art to process any given polymer. For example, because of the reduction in viscosity that occurs in a polymer melt as the temperature is raised,

the throughput of a given polymer through a given piece of processing equipment can be raised as temperature is raised. In the absence of macromolecular disentanglement, a polymer could conceivably be processed at an unconventionally low temperature, for example to be able to incorporate a thermally sensitive additive, but the throughput of the equipment being used to process the polymer must necessarily be lowered, and the power required to extrude the melt must increase significantly, which explains why such blends are never processed that way commercially.

0029. The present invention overcomes the limitation on throughput that is inherent in prior attempts to incorporate thermally sensitive additives into polymers by lowering temperature, by providing a molecularly disentangled polymer that has a viscosity that allows increased throughput compared to non disentangled polymer.

0030. The conventional processing conditions for a single screw extruder are exemplified in "Plastics Extrusion Technology Handbook" (xx, table 2-1, page 44) and shown in table 1.

Table 1  
Typical Production Rates for Single Screw Extruders

Barrel Diameter (cm)	L/D	rate (kg/sec)
3.81	24:1	0.0063 - 0.0076
5.08	24:1	0.0113 – 0.0151
6.35	24:1	0.0189 – 0.0315
8.89	24:1	0.0378 – 0.0504
8.89	30:1	0.0441 – 0.0567
11.43	24:1	0.0882 – 0.126
15.24	24:1	0.1512 – 0.2016

0031. Table 1 is shown as an example of the approximate throughputs can that be obtained on single screw extruders with non molecularly disentangled polymer within the conventional melt temperature range, defined below.



0032. The “conventional melt temperature range” (CMTR) at which a polymer is processed is defined herein as that temperature range within which one skilled in the conventional art would expect to have to use to fabricate articles that comprise the polymer, at throughputs that would be expected by one skilled in the present art, under conventional processing conditions and normally at throughputs which are economically feasible. Table 1 gives a list of common polymers and their CMTR's. Although those skilled in the art may use CMTR's that differ slightly from the data in table 2, for the purposes of this invention, and the disclosure of melt temperatures herein, the values of table 1 should be used for the polymers listed there.

0033. The “conventional throughput” of a process refers to the throughput of polymer melt that would be obtained in a processing or blending equipment from non disentangled polymer at a conventional melt processing temperature

Table 2  
Conventional Melt Temperature Ranges

Polymer	Range ( °C)
Polyethylene (PE)	180 – 220
Polypropylene (PP)	205 – 235
Polycarbonate (PC)	265 – 315
Polyamide (PA)	270 – 300
Polystyrene (PS)	220 – 240
Polyethylene Terephthalate Glycol (PETG)	260 – 280
Polyethylene Terephthalate	250 - 275
Polymethyl Methacrylate (PMMA)	220 – 240

0034. The term “substantially degraded” is used herein to describe the state of an additive after significant changes to the molecular or physical structure of the additive have taken place after the additive has been subjected to the temperature of extrusion of a polymer into which the additive has been

blended. Optionally, changes to the polymer may take place as fragments of the additive would react with the polymer.

0035. For many additives, a change in physical or chemical state is expected to take place during incorporation into a blend. For example phosphites used as process stabilizers are known to be oxidized to phosphates, and part of the art of stabilizing polymers lies in selecting formulations that degrade in a controlled way. In the context of the present invention, the changes that are being referred to when an additive becomes degraded are undesirable, as in the examples given above as background. A significant change is one that takes place to the extent that an additive becomes unsuitable for use for the purpose for which it was intended.

0036. The terms “nanoparticles”, “nanoclays”, and “organoclays” are used interchangeably herein. By “nanoparticles”, is meant particles with a largest dimension (e.g., a diameter) of less than, or less than or equal to about 750 nm (nanometers). Also incorporated and included herein, as if expressly written herein, are all ranges of particle sizes that are between 0 nm and 750 nm. It should be understood that every limit given throughout this specification will include every lower, or higher limit, as the case may be, as if such lower or higher limit was expressly written herein. Such particles are technologically significant since they are utilized to fabricate structures, coatings, and devices that have novel and useful properties due to the very small dimensions of their particulate constituents. Nanoparticles with particle sizes ranging from about 2 nm to about 750 nm can be economically produced. Non-limiting examples of particle size distributions of the nanoparticles are those that fall within the range from about 2 nm to less than about 750 nm, alternatively from about 2 nm to less than about 200 nm, and alternatively from about 2 nm to less than about 150 nm. It should also be understood that certain ranges of particle sizes may be useful to provide certain benefits, and other ranges of particle sizes may be useful to provide other benefits (for instance, color enhancement requires a different particle size range than the other properties). The mean particle size of various types of particles may differ from the particle size distribution of the particles. For

example, a layered synthetic silicate can have a mean particle size of about 25 nanometers while its particle size distribution can generally vary between about 10 nm to about 40 nm. (It should be understood that the particle sizes that are described herein are for particles when they are dispersed in an aqueous medium and the mean particle size is based on the mean of the particle number distribution.

0037. Non-limiting examples of nanoparticles can include crystalline or amorphous particles with a particle size from about 2 to about 750 nanometers. Boehmite alumina can have an average particle size distribution from 2 to 750 nm. Nanotubes can include structures up to 1 centimeter long, alternatively with a particle size from about 2 to about 50 nanometers.

0038. Some layered clay minerals and inorganic metal oxides can be examples of nanoparticles, and are also referred to herein as "nanoclays". The layered clay minerals suitable for use in the present invention include those in the geological classes of the smectites, the kaolins, the illites, the chlorites, the attapulgites and the mixed layer clays. Typical examples of specific clays belonging to these classes are the smectices, kaolins, illites, chlorites, attapulgites and mixed layer clays. Smectites, for example, include montmorillonite, bentonite, pyrophyllite, hectorite, saponite, sauconite, nontronite, talc, beidellite, volchonskoite and vermiculite. Kaolins include kaolinite, dickite, nacrite, antigorite, anauxite, halloysite, indellite and chrysotile. Illites include bravaisite, muscovite, paragonite, phlogopite and biotite. Chlorites include corrensite, penninite, donbassite, sudoite, pennine and clinochlore. Attapulgites include sepiolite and polygorskyte. Mixed layer clays include alleverdite and vermiculitebiotite. Variants and isomorphic substitutions of these layered clay minerals offer unique applications.

0039. Layered clay minerals may be either naturally occurring or synthetic. An example of one non-limiting embodiment of the nanoclay particle used herein uses natural or synthetic hectorites, montmorillonites and bentonites. Another embodiment uses the hectorites clays commercially available, and typical sources of commercial hectorites are the LAPONITES.TM. from Southern Clay

Products, Inc., U.S.A; Veegum Pro and Veegum F from R. T. Vanderbilt, U.S.A.; and the Barasym, Macaloids and Propaloids from Baroid Division, National Read Comp., U.S.A.

0040. Natural clay minerals typically exist as layered silicate minerals and less frequently as amorphous minerals. A layered silicate mineral has  $\text{SiO}_4$  tetrahedral sheets arranged into a two-dimensional network structure. A 2:1 type layered silicate mineral has a laminated structure of several to several tens of silicate sheets having a three layered structure in which a magnesium octahedral sheet or an aluminum octahedral sheet is sandwiched between two sheets of silica tetrahedral sheets. In some embodiments, it may be desirable for the coating composition to comprise a plurality of nanoparticles that comprise types of (or a first group of) nanoparticles other than 2:1 layered silicates. It should be understood that such a group of nanoparticles refers to the type of nanoparticles, and such nanoparticles may be distributed throughout the coating composition in any manner, and need not be grouped together. Also, even in these embodiments, the coating composition may comprise at least some (possibly a non-functional amount) of nanoparticles comprising 2:1 layered silicates (which may comprise a second group of nanoparticles).

#### Preparation of Polymer Melt

0041. Any polymer melt of which the product of the invention comprises is prepared preferably in a mixing and heating apparatus which can supply heat and shear to solid polymer in order to render it in a viscous state and able to be further processed. The melt can be formed from virgin polymer, for example in the form of pellets, or as previously disentangled polymer, where the polymer has been macromolecularly disentangled in the sense described above, and then frozen into the solid state by cooling. The additive can also be a polymer melt and prepared in the same way as the polymer melt into which it is blended. A polymer melt can also comprise more than one polymer.

0042. Any mixing and heating apparatus and method which is known by those skilled in the art can be used in the invention, and particularly preferred mixing and heating apparatus and methods are extrusion apparatus and

processes. Extrusion processes are well known in the art, and any suitable extrusion process can be used to prepare the polymer melt of the present invention, using the guidelines provided herein. These extrusion processes usually comprise means for feeding materials to the extruder, means for melting and mixing materials, means for transporting the molten materials to a forming die, and means for cooling the molten sheet or string of polymer formed thereby to form a product. In case a second film, string or web is laminated to the molten sheet or string, such second film or web may participate in the cooling process. All means mentioned in this paragraph and known to those skilled in the art or later discovered are contemplated for use in the invention.

0043. Methods and apparatus suitable for feeding the raw materials to the extruder generally are known. A preferred feeding means comprises a conveying mechanism such as a vacuum pump connected to a vacuum pipe, the pipe being submerged in a reservoir of polymer material. In a controlled manner the pump generates vacuum in the pipe causing the pipe to suction polymer from the reservoir and to deposit it in a feed hopper. The feed hopper typically contains a metering device that deposits accurately controlled amounts of polymer into the extruder receiving cavity. Multiple cavities and feed hoppers may be present in a single extruder thereby enabling feeding of multiple components. In addition, antistatic and vibratory devices can be positioned at or near the feed hoppers to assist in accurately dosing the polymer. Other feeding means known to those skilled in the art or later discovered also are contemplated for use in the present invention.

#### Preferred Embodiments

0044. The embodiments of the invention can be best understood by reference to the figures.

0045. In figure 1 is shown a block diagram of an embodiment of the invention. A polymer melt, prepared according to the guidelines mentioned above, is fed into a means for molecularly disentangling the molecular chains of the melt (10). The means for disentanglement can comprise any method for applying to

the melt a mechanical vibration in either shear or compressive and that causes the melt to undergo a reduction in viscosity. The preferred embodiment of the invention uses the process and apparatus described in U.S. patent numbers 5,885,495 and 6,210,030 respectively. The apparatus is available under the name "Tek Flow processor" from Stratek Plastic Ltd. (Dublin, Ireland), however the invention is not to be construed as being limited to this embodiment or particular apparatus.

0046. In summary of the process of the '495 patent, the frequency of oscillation, the speed of motion of the dragging surfaces, the amount of extensional strain and acceleration present, and the temperature of the melt all interact to determine the proper state of elasticity in the molten polymer to enable disentanglement to take place. In general, because of the time-temperature superposition principle (applied to melt relative elasticity) which makes working at high frequency and high temperature or low frequency and low temperature equivalent, and because of the relatively easier practical realization of a vibrating system working at low frequencies (1 to 100 Hz), disentanglement is done at a melt temperature well within the rubbery flow region of the polymer, and at temperatures that are below the CMTR of the polymer. Throughputs that are still typical of conventional processing conditions can still be obtained at these lower temperatures by virtue of the reduction in viscosity of the melt by disentanglement.

0047. For example, low temperature disentanglement of Polycarbonate is carried out at  $T = 200\text{--}215\text{ }^{\circ}\text{C}$  (*versus*  $265\text{--}315\text{ }^{\circ}\text{C}$  CMTR for conventional processing). For Polypropylene, a temperature between  $135\text{ }^{\circ}\text{C}$  and  $165\text{ }^{\circ}\text{C}$  can be used (*versus*  $205\text{--}235\text{ }^{\circ}\text{C}$  CMTR conventionally). For PETG:  $160\text{ }^{\circ}\text{C}$  (*versus*  $260\text{ }^{\circ}\text{C}$  conventionally), and more generally, for any given melt, a temperature saving of up to  $100\text{ }^{\circ}\text{C}$  is obtained.

0048. Referring again to figure 1, the melt that is supplied to the means for disentangling (10) is preferably non disentangled, in which case it will be at any temperature that is suitable for melt transfer into the means for disentanglement, but probably within the CMTR of the polymer.

0049. The molecularly disentangled melt is then transferred to a means for premixing the additive and disentangled polymer prior to being fed to a means for blending (12). In the premixing step (11), one or more additives are supplied, and the polymer melt and additives are pre-dispersed before the blending step (12), however, pre-dispersion is optional and may be unnecessary, for example in the case where the additive is itself a melt, or has a melting point below the temperature of the disentangled melt and does not require pre-dispersion prior to the shearing of the blend in order to assure an homogenous dispersion.

0050. Figure 2 shows the preferred embodiment of the invention in which more than one disentanglement station is used. An extruder (20) is used to feed polymer melt to a disentanglement station (21), from which the melt is fed to a mixing station (23). Additives are supplied through a continuous metering section (22) also into the mixing station. In this embodiment of the invention, the mix of disentangled polymer and additives is supplied to a second disentanglement station (24), where vibratory shear under extension applied to the melt at relatively low temperature is sufficient to cause optimum conditions for the dispersion of the additive and polymer to take place. The blend can then go on to subsequent processing or shaping operations, or be cooled and pelletized in preparation for being used subsequently.

0051. In this preferred embodiment of the present invention, the overall machine would consist of two disentanglement processors, as described above, connected head to tail through a mixing station, where a second component (an "additive"): another polymer, a liquid, a paste, a powder, a melt etc. is fed through a feeding mechanism such as another extruder, an Archimedes' screw, a gear pump, a vacuum loader etc., or any other feeding device known to the art of feeding two materials for mixing. The presence of the second disentanglement processor, (24) of Fig. 2, is particularly useful for optimizing dispersion of the additive in the mix, and, in the case of nanoclays, optimizing exfoliation as well as dispersion.

0052. The invention is not to be construed as being limited by the examples given above in the figures. For example, disentangled polymer can be

pelletized and stored, and then re-melted and extruded and blended with additives. The disentanglement station therefore does not have to be co located with the blending station.

0053. Any such arrangement of the process steps and process equipment in which additive is blended with disentangled polymer is therefore to be considered as an embodiment of the present invention, and one skilled in the art will be able to devise methods for handling and processing the components that go to make up the blend.

#### Examples

0054. The invention can be understood further by reference to the examples described below.

#### Example 1

0055. The following example describes the mixing of maple wood flour with polypropylene. It shows the ability to disperse the maple wood flour into a polypropylene which has a medium melt flow index 15.0 g/10min (230°C/2.16kg), without the use of processing aids for reducing viscosity, at a temperature of 160°C, which is well below the usual polypropylene processing temperature of 230°C and well below the wood degradation temperature of 200°C.

0056. The wood flour can be added as is, or after dipping it into an emulsion of polyurethane latex, drying and curing it, to obtain a latex coated wood flour. The arrangement of figure 2 was used for the experiment. The maple wood flour was dried at 90°C for 2 hours prior to processing. Before introducing the wood flour into the polypropylene, the PP was treated in the TekFlow processor (21) to reduce its viscosity and temperature. The dried maple wood flour was introduced into the polypropylene using a vertical co-extruder at the entrance, (23), of the second treatment station, (24). The temperature of the co-extruder was set at 160°C.

0057. The extruded blend exited the co-extruder as a strand. It was air cooled, collected then pelletized. The maple wood flour loading in virgin polypropylene was about 15% in this example, but can be easily increased to higher loading percent by increasing the RPM of the co-extruder.



### Example 2

0058. The following example describes the mixing of polyaniline powder with polyethylene terephthalate glycol (PETG). It shows the ability to disperse the polyaniline into the PETG at a temperature of 160°C, which is well below the usual PETG processing temperature of 260°C and also well below the polyaniline temperature of degradation of 230-240°C.

0059. The arrangement of figure 2 was used, and the numbers in parentheses refer to that figure. The PETG was first introduced into a TekFlow processor (21) at 265°C via an extruder (20). (all temperatures of the extruder zones were also at 265 °C). The melt continued through (23) and (24), initially also at 265 °C. The plastic melt was submitted to mechanical extensional shear vibration in both disentanglement stations, with minimum or no external pressure in (23), at a constant amplitude and frequency, specific to each station. The viscosity of the plastic melt was quantitatively followed by measuring the torque required to turn the shaft at given RPM. As the viscosity of the melt reduced, the temperatures in the 1<sup>st</sup> and 2<sup>nd</sup> treatment stations and in the mix station,(23) were gradually decreased to 160°C (with temperatures on the extruder always remaining at 265°C). When the temperature in all the zones of the disentanglement stations had decreased to 160°C, then the additive feeder containing the polyaniline powder was activated. The additive feeder introduced the polyaniline at the entrance,(23), of the second treatment station (24). The extruded blend came out of the die as a flat strip. Visual inspection and measurement of electrical conductivity showed that the introduction of polyaniline was uniform and successful.

### Example 3

0060. The following example describes the mixing of nanoclay particles with polypropylene. It shows the ability of dispersing the nanoclay particles into a polypropylene which has a medium melt flow index 15.0 g/10min (230°C/2.16kg), at a temperature of 160°C, which is well below the usual polypropylene

processing temperature of 230°C and well below 190°C, which is the temperature of organic decomposition of the coating on the nanoclay particle.

0061. Referring again to figure 2, the polypropylene was first introduced into the TekFlow processor at 205°C (all temperatures from extruder to 1<sup>st</sup> and 2<sup>nd</sup> treatment stations were at 205°C). The plastic melt in both of the treatment stations were submitted to mechanical extensional shear vibration, with minimum or no external pressure in (23), at a constant amplitude and frequency, specific to each TekFlow station. The viscosity of the plastic melt being reduced, the temperatures in the 1<sup>st</sup> and 2<sup>nd</sup> treatment stations were gradually decreased to 160°C (temperatures on the extruder always remain at 205°C).

0062. The nanoclays were introduced into the polypropylene using a vertical co-extruder. The temperature of the co-extruder was set at 160°C.

0063. When the PP melt reached 160°C in the first treatment station, then the co-extruder was started at a speed of 10 RPM. The co-extruder introduced the nanoclay into an inlet chamber located just before the entrance of the second treatment station. The extruded blend came out as a strand. It was air cooled, collected then pelletized. The nanoclay content was determined using thermogravimetric analysis (TGA) by heating from room temperature (RT) up to 800°C (to remove the PP matrix) and then cooled back down to RT. The weight of the sample is recorded during the complete test and the final weight indicated the nanoclay content.

0064. The TGA results indicated that the amount of pure nanoclay loading in the mix with polypropylene, without the weight of the binder, was about 12%.

0065. X-Ray diffraction (XRD) was used to evaluate the degree of dispersion and the level of exfoliation of the platelets in the blended mixture. XRD was carried out on both the original nanoclay and on the dispersed nanoclay in the PP matrix. The diffraction peak corresponding to the inter-distance between platelets was quite visible in the X-Ray spectrum of the original nanoclay. This peak was no longer visible in the nanoclay dispersed in polypropylene. The shift to lower angle of the diffraction peak, to the extent that it is no longer observed, is

an indication of the increase in efficiency of exfoliation (i.e. separation of the layers of the nanoclays) due to the new invention.

#### Example 4

0066. Homogeneous Blends of controlled MWD were obtained from mixing grades of different Melt Flow Index.

0067. In this example two additive-free linear polycarbonate grades of very different melt flow indices (MFI), respectively 78 and 4.2 (g/10 min, 1.2 Kg at 300°C) were dispersed into one another in different proportions (10 to 90%). The low MFI plastic melt was subjected to mechanical extensional shear vibration in a first TekFlow processor at a constant amplitude and frequency to produce a significant viscosity decrease (an increase of its MFI) by disentanglement. When steady state conditions were reached, the high MFI grade was introduced via an extruder at a temperature of 200°C, into a mixing chamber, where it was mixed with the disentangled melt produced by the first TekFlow processor. The second TekFlow processor uses its own specific shaft rotation and vibration frequency and amplitude to continue to disentangle the blend and disperse it under optimum conditions.

0068. As explained in the previous examples, the temperatures in the zones of the first and second TekFlow processors were gradually lowered to their steady state value, respectively 215 °C and 235 °C, from an initial value of 285°C for both (which remained the temperature in the extruder).

0069. The extruded blend came out as a strand. It was air cooled, collected, and then pelletized.

0070. Blends produced by this invention are homogeneous and indistinguishable from conventionally produced grades in reactors. They are totally transparent and can be injection molded. A Gel Permeation Chromatography (GPC) study shows no tendency for bimodality, at all proportions. Their  $M_w$  varies like the arithmetic average of the two grades'  $M_w$ , as established by their proportion in the blend, and the MFI of the blends varies like the -3.4 power of the weight molecular weight average,  $M_w$ , making it possible to

produce any grade of chosen MFI between 78 and 4.2 , by simply changing the speed of rotation of the screw of the co-extruder feeder, (22).

0071. The high MFI PC grade introduced in the hopper of the co-extruder could also be pre-mixed with thermally sensitive additives. The low MFI grade can be a linear or a branched Polycarbonate, or a mix of the two. Temperature is maintained low in the second TekFlow station, adjusted downwards if thermally sensitive additives are pre-mixed with the high MFI grade.

The high MFI PC grade could also be replaced with a polymer from a different family, Acrylonitrile Butadiene Styrene (ABS), Polybutadiene terephthalate (PBT), Polyethylene terephthalate (PET), or even other polymers usually considered incompatible with the polycarbonate family, such as polyolefins. Incompatible polymers have polymer chains with chemical groups which do not interact well, resulting in the formation of larger segregated blocks, with weak interfaces, for the morphological phases which form during melt blending. The result of submitting such blends to the treatment according to the present invention is a better dispersion of the segregated phases, which means a break up into smaller segregated blocks , a better interpenetration of adjacent macromolecules in the interface between the segregated phases,, allowing a better interaction between the chemical groups and thus better compatibility. The better the compatibility the better the mechanical performance of the blend.

0072. Polymers and copolymers that can be processed with the invention include but are not limited to; ethylene propylene copolymer, high-density polyethylene, high-impact polystyrene, low-density polyethylene, polyamide, polyacrylic acid, polyamide-imide, polyacrylonitrile, polyarylsulfone, polybutylene, polybutadiene acrylonitrile, polybutadiene styrene, polybutadiene terephthalate, polycarbonate, polycaprolactone, polyethylene, polyethyl acrylate, polyetheredierketone, polyethylene sulfone, polyethylene terephthalate, polyethylene terephthalate glycol, polyimide, polyisobutylene, polymethyl acrylate, polymethyl ethyl acrylate, polymethyl methacrylate, polyoxymethylene (polyacetal), polyphenylene ether, polyphenylene oxide, polyphenylene sulfide, polypropylene terephthalate, polystyrene, polytetrafluoroethylene, polyurethane, polyvinyl alcohol,

polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polyvinylidene fluoride, polyvinyl methyl ether, polyvinyl methyl ketone, styrene butadiene, styrene butadiene rubber, cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, cellulose nitrate (celluloid), chlorinated polyethylene, chlorotrifluoroethylene, ethylene acrylic acid, ethylene butyl acrylate, ethyl cellulose, and polymers and copolymers of acrylonitrile butadiene acrylate, acrylonitrile butadiene styrene, acrylonitrile, chlorinated PE and styrene, acrylonitrile methyl methacrylate, acrylonitrile, acrylonitrile styrene, acrylonitrile, butadiene acrylonitrile, ethylene propylene diene monomer,

0073. While the description and examples of the present invention presented above have been limited to certain embodiments, it is recognized that similar advantages over the existing art will be obtained by other embodiments. It will be obvious to those skilled in the art that various changes and modifications can be made without departing from the spirit and scope of the present invention, and it is intended to cover the claims appended hereto. All such modifications are within the scope of this invention.